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SEA-LEVEL MONITORING OF THE INCINERATION OF ORGANIC CHLORIDE WASTE BY M/T VULCANUS IN THE NORTHERN GULF OF MEXICO SHELL WASTE BURN NUMBER 2

Tereco Corporation

PREPARED FOR
Environmental Protection Agency

10 January 1975

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PB 253 365

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TO

THE ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C.

ATTN.: T. A. Wastler

BY

TERECO CORPORATION
COLLEGE STATION, TEXAS

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

CONTRACT NO. 68-01-2829

JANUARY 10, 1975

TERECO CORPORATION

Man's Role in the Biosphere

ECOLOGICAL SYSTEM ANALYSTS
Environmental Assessments

SOCIO-ECONOMIC IMPACTS

GLOBAL OCEANOGRAPHIC STUDIES
Coastal Zone to the Abyss

January 10, 1975

Mr. T. A. Wastler
Project Officer, Contract 68-01-2829
U.S. Environmental Protection Agency
401 M Street, SW (WH-448)
Washington, D. C. 20460

Dear Mr. Wastler:

Please find attached TerEco Corporation's report on the marine survey project carried out under Contract No. 68-01-2829. We have titled our report "Sea-level Monitoring of Organic Chloride Waste by M/T VULCANUS in the Northern Gulf of Mexico."

For the record, I wish to stipulate that the following persons connected with TerEco played some role in carrying out the terms of this contract:

B. M. James, Ph.D. - Chief Scientist on ORCA
H. O. Hartley, Ph.D. - Statistical Analysis
C. Hill, M.S. - Loran and Radar Operator
R. DuBois - Sampling Chief
J. Bennington - Sampling Aide
J. Trefrey - Chemist, Chlorinity Determinations
R. Sims - Chemist, Alkalinity Determinations
K. Grisham - Report Aide
W. E. Pequegnat, Ph.D. - Project Supervisor

Vernon Crotts - Under Lease, Master, M/V ORCA

I wish to acknowledge with appreciation the aid given TerEco by two EPA scientists, viz., Richard Ross and - especially - Robert Vickery, who is an accomplished sea-going biologist.

Permit me to call your attention to the fact that TerEco personnel have spelled out a few recommendations at the end of the report for procedures that you might wish to include in the protocol of possible future monitoring efforts. We are prepared to elaborate upon some of these if and when you may deem it advisable.

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TERECO CORPORATION
500 University West
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In closing I wish to assure you that TerEco is pleased to have had an opportunity to participate in this historic effort. In view of the fact that we found no adverse effects on the marine environment resulting from Research Burn 2, it is our judgment that carefully controlled incineration at sea is the solution to some otherwise difficult problems of industrial waste disposal. At this writing the open ocean promises to be a better staging area for this effort than the land.

I wish also to thank you and Mr. Ed McLean for your kind cooperation and effective management of this project.

Sincerely yours,

Willis E. Pequegnat
President

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INTRODUCTION

OUTLINE OF U.S. INVOLVEMENT IN OCEAN INCINERATION

Early in 1974 serious concern began to mount within the U.S. Environmental Protection Agency with regard to possible degradation of the marine environment resulting from the practice of dumping into the open ocean certain untreated organic chloride wastes derived from the manufacture of vinyl chloride.

Made aware of EPA's growing concern in this matter, Shell Chemical Company began to explore alternative methods for the disposal of these wastes during the interval when a land-based incinerator could be fabricated and put into use. The most promising of these alternatives appeared to be incineration of the wastes at sea aboard an incinerator ship such as M/T VULCANUS. The VULCANUS had already carried out several successful incinerations in European waters of wastes approximately the same as those produced in this country by Shell. The results of these European burns were so good, showing that more than 99 percent of the waste was transformed into HCl and carbon dioxide, that Shell commissioned VULCANUS to incinerate some 16,000 metric tons of organic waste in storage in Houston, Texas. VULCANUS arrived in Houston in September 1974, but the first burn did not take place in the Gulf of Mexico until October 20-28, 1974.

THE FIRST PUBLIC HEARING: RESEARCH BURN 1

Following considerable internal discussion and debate with outside groups vitally interested in the welfare of the environment, the Environmental Protection Agency accepted responsibility for controlling ocean incineration practices. Accordingly the Agency scheduled an open hearing to test public reaction to Shell's request for a permit to burn the chloride wastes then in storage. This first public hearing on incineration of organic wastes at sea was scheduled for 4 October 1974 in the Shamrock Hilton Hotel in Houston, Texas.

On September 29 Shell retained TerEco Corporation to provide expert testimony at this hearing and to draft a plan for monitoring the burn at sea should a permit be issued. Pursuant to the hearing, EPA granted research

permit 730D008C to Shell Chemical Company to burn 4000 metric tons of organic chloride wastes produced in the Shell Deer Park Manufacturing Complex. This incineration, which was to be carried out by VULCANUS in a new incineration site some 165 statute miles southeast of Galveston, has come to be called Research Burn 1.

One of the provisions of the permit required that Shell conduct a sea level monitoring program to determine whether or not the products of combustion would affect the marine environment adversely.

SEA-LEVEL MONITORING BY TERECO

Shell Chemical Company was required to carry out an extensive monitoring program in addition to that which EPA planned to conduct aboard OREGON II and by aircraft. Shell commissioned TerEco to carry out that part of its monitoring program dealing directly with possible changes in the sea water and its biota. Meanwhile, Shell conducted monitoring of stack gases aboard the M/T VULCANUS. TerEco conducted its field work during the period from 21 to 23 October (the actual burn ran from 20-28 October) and provided preliminary data to Shell within one week. A more formal report entitled "A Field Monitoring Study of the Effects of Organic Chloride Waste Incineration on the Marine Environment in the Northern Gulf of Mexico" was submitted to Shell on 14 November 1974. In general it was concluded that there were no detectable changes in the pH of the sea water under the incineration gas plume discharged by VULCANUS. Moreover, no changes were detected in phytoplankton counts or diversity between test and control stations. These conclusions were based upon a rigorous statistical analysis.

THE SECOND PUBLIC HEARING AND RESEARCH PERMIT

Pursuant to submission of Shell's report and completion of its own findings, the Environmental Protection Agency decided to hold a second public hearing in Houston, Texas before acting upon Shell's request for a permit to burn the remaining 12,000 metric tons of waste. This meeting was held on 14 November 1974, again in the Shamrock Hilton Hotel. On this occasion Dr. Bela M. James represented TerEco. Somewhat vitriolic public comments on some aspects of the monitoring of the first burn

motivated EPA to concentrate efforts on carrying out an indisputably good monitoring program for the second burn both in the air and simultaneously aboard VULCANUS and ORCA. On 26 November EPA authorized Shell to incinerate 4200 metric tons under permit No. 730D008C(2) (which became effective on 28 November). Again sea-level monitoring was required.

MONITORING RESEARCH BURN 2

On Tuesday, November 26, 1974, T. A. Wastler of EPA requested TerEco to carry out a sea-level monitoring of the second burn.

A meeting of Shell, EPA, and TerEco personnel was held at the Deer Park Complex on Saturday, November 30 in order to discuss and coordinate the total monitoring program. VULCANUS was loading waste at the time and was ready to set sail within a matter of hours. TerEco was to outfit for its part of the program and sail by noon on Monday, December 2. On December 2, also Mr. Ed McLean of EPA and W. E. Pequegnat of TerEco met in the Houston Intercontinental Airport in order to sign the contract just prior to ORCA's departure.

REPORT ON RESULTS OF SECOND BURN

On 10 December 1974 a meeting was convened in the Region VI offices of EPA in Dallas for the purpose of advising regional officials and representatives of the governments of Texas, Louisiana, Mississippi, Alabama, and Florida of the preliminary results of the monitoring of Research Burn 2. All monitoring data presented supported the conclusion that incineration of organic chloride wastes by VULCANUS was not adversely affecting the marine environment in ways detectable by current methods of monitoring (including the time frame). The results produced by TerEco aboard ORCA and presented at the Dallas meeting by Robert Vickery are presented in detail in the following sections of this report.

OBJECTIVES OF THE SEA-LEVEL MONITORING PROGRAM

At the Deer Park Complex meeting of 30 November, T. A. Wastler provided TerEco with an outline of the monitoring program to be carried out aboard ORCA. This document is attached herein as Appendix A.

The overriding objective was to determine whether or not

the combustion products derived from the burned chlorides caused any changes in sea water that could be construed as being deleterious to marine life. In order to achieve this, three operational objectives were defined, as follows:

1. PLUME IDENTIFICATION

This refers specifically to detecting the location and dimensions at sea level of the cloud (often invisible) of gases (plume) produced by VULCANUS. It should be noted here that after achieving combustion temperature the fire in the incinerators is maintained by feeding only the organic chloride waste. The principal components of the gas plume are HCl, CO_2, Cl_2, and H_2O. From time to time locating the plume was facilitated by release of NH_3 forward of the incinerator stacks.

2. DETERMINATION OF IMMEDIATE EFFECTS OF COMBUSTION GASES

Identification of the plume and locating it downwind of VULCANUS increased the scientific effectiveness of attempts to determine the immediate effects of fallout on surface sea water. Accordingly during some test runs of ORCA surface water samples were taken at the moment HCl was detected in the air at deck level.

3. DETERMINATION OF LONG RANGE EFFECTS OF COMBUSTION GASES ON THE BIOTA

Considering the dynamic relationships between small marine organisms and their sea water milieu, it was deemed feasible to gain insights into possible long range effects of combustion fallout by sampling the surface and near-surface biota (neuston) continuously for one hour and then subjecting them to rigorous chemical analysis for any increases in trace metals and organic chlorides.

SAMPLING REGIMEN

SHIP MOVEMENTS AND POSITIONING

When results of sampling are presented in a later section of this report, it will become clear that VULCANUS was always the point of reference

associated with the wind that determined the deployment and pattern of movement of ORCA. But it should be noted here that Loran readings were utilized for more or less discrete positioning of both ORCA and VULCANUS, a parameter that was important to ensure that both vessels (particularly VULCANUS) remained within the approved incineration site, whereas Radar was utilized to ascertain the distances and angles of ORCA from VULCANUS during plume search and sampling activities.

DEFINITIONS OF TERMS (see Appendix A Figs. 1, 2 and 3 for sampling patterns)

1. Plume Search Runs.- These ship tracks, of which there were two in the present monitoring series, involved zig-zag movements of ORCA downwind of VULCANUS and at right angles to wind flow in order to mark the positions at which an odor of HCl was detectable by personnel stationed on the bow (e.g., see Fig. 1).

2. Test Runs.- These refer to the paths, always downwind of VULCANUS, taken by ORCA when sampling was being carried out for immediate or long range effects of plume fallout. Four test runs were carried out by ORCA in the Research Burn 2 monitoring series.

3. Control Runs.- Control runs generally had the same mission as test runs except that they were always carried out upwind of VULCANUS. There were three control runs in this monitoring; they are related to tests as follows:

Test Run I	-	Control Run I
Test Run II	\	Control Run II
Test Run III	/	
Test Run IV	-	Control Run III

4. Times and Sequence of Runs.- It should be noted that sampling was carried out throughout a 24-hour period, that is, involving both day and night sampling. This is shown in the following:

Run	Hours
Test Run I	2222 to 0102
Control Run I	0142 to 0221
Test Run II	1104 to 1404
Control Run II	1447 to 1527
Test Run III	1630 to 1703

FIELD SAMPLING OF AIR AND WATER

AIR

Aboard ORCA sampling of air for HCl was accomplished simply through detection of odor by human olfaction. The HCl monitor installed aboard the ship proved to be unreliable early on in the test; hence this alternative method of HCl was utilized during Plume Search Runs. During the zig-zag traverses of Plume Search 1 and the arc traverses of Plume Search 2, two or more persons were stationed on ORCA's bridge-deck facing into the wind. At the instant they detected the HCl odor, they signaled the Radar operator to read bearing and distance parameters on VULCANUS. In Test Run II water samples for pH, chlorinity, and alkalinity determinations were taken only when sniffers detected HCl in the air.

Actually the use of human olfaction for HCl detection in minute amounts is far from unreliable. The average human being is able to detect gaseous HCl in concentrations of only a few parts per million ($\sim$ 5 ppm).

WATER

Determinations of values for pH, chlorinity, and alkalinity were done only for surface waters. Test water was collected from the surface using a two-gallon polyethylene bucket slung from a nylon rope. This permitted samples to be taken while ORCA was underway--a factor that not only increased the degree of sampling synopticity but also decreased chances of contaminating samples with ship effluents. In addition water samples, collected as above, were analyzed for organic chlorides, copper and zinc.

INDIGENOUS BIOTA

Zooplankton

Zooplankton samples were collected with a neuston net. This net consists of a rectangular aluminum frame, measuring 1 X 2 m, to which a nylon bag 10 m long and of 1 mm mesh is attached. The net was weighted to ride just below the surface in order to avoid collecting large amounts of tar balls, plastics, and other extraneous materials commonly encountered in surface waters of all oceans. It was towed at approximately 3 knots. Upon retrieval, the sample was drained and transferred with some fluid to a glass jar in which it was frozen for shore analysis.

Phytoplankton

Phytoplankton samples were collected with a Hansen type net having a mouth opening of 20 cm, a length of 1.5 m, and a 35 micron mesh. It was towed just under the surface at 3 knots. Samples were stored in glass jars and frozen for shore analysis.

LABORATORY METHODS

ABOARD SHIP

THE RECIPROCAL OF HYDROGEN ION CONCENTRATION

The only analysis conducted aboard ORCA was pH. Determinations were generally made within eight minutes after collection. A Corning Model 112 digital pH meter standardized at pH 9.180 was utilized. Sample and buffer temperatures were always within 1°C at 23.7° $\pm$ 0.5°C. During the analyses conducted for Test Run 1 and Control Run 1 the line voltage variation caused the meter to fluctuate $\pm$ .01 pH unit. During the remainder of the pH determinations, the instrument was connected to a 12 volt lead-acid battery via a 110 volt transistorized inverter. Fluctuations of the instrument were reduced to a maximum of $\pm$ .003 pH units.

SHORE LABORATORY

CHLORINITY

Water samples were placed in thoroughly rinsed 8 ounce bottles, tightly capped and returned to the shore laboratory for analysis. The Mohr titration method was utilized. This is based upon the differential solubilities of the Cl^- ion and $CrO_4^=$ ion with Ag^+ ion. Initially the chloride ions are precipitated by silver due to their lower solubility. When chloride is depleted, the $CrO_4^=$ reacts with silver to form a red precipitate, the appearance of which signals the end point of titration. Samples are compared with Copenhagen standard sea water to obtain chlorinity values.

A standard working curve was generated by using dilutions of Copenhagen standard sea water (19.3755 ppt Cl). The precision of this method is $\pm$ .03 ppt. Additional information on the titration technique is given in Appendix B.

ALKALINITY

Water samples collected on Test Run II and Control Run II were analyzed for total alkalinity. A potentiometric titration method using mathematical determination of end points was utilized. Additional information on the technique employed is given in Appendix B.

ORGANIC CHLORIDE, COPPER AND ZINC ANALYSES

Water samples for organic chloride, copper and zinc determinations were collected from the surface by means of the polyethylene bucket.

Organic chloride samples were placed in acetone-washed quart glass bottles and sealed with teflon-lined caps.

Water samples collected for copper and zinc analyses were placed in quart polyethylene bottles to which 2 ml of redistilled concentrated nitric acid had been added as a preservative. These samples were analyzed in the laboratories of Shell Development Company.

The frozen zooplankton and phytoplankton samples were also analyzed for organic chlorides and metals by Shell.

Zooplankton samples were thawed and separated into liquid and solid portions. These were then analyzed separately. The organic chloride limit of detection in the liquid was 0.025 ppm. However, due to the small sample size, the detection limit for organic chlorides in the solid (organismic) portion was 3 ppm.

In the case of phytoplankton analyses, the paucity of organisms in the sea water and thus the samples argued against separate analyses of water and organisms. The organic chloride detection limit for the whole sample is estimated to be 3 ppm.

PRESENTATION AND DISCUSSION OF RESULTS

PLUME DEMARCATION

OBJECTIVE

As indicated previously, the principal reason for sea level plume identification was to ascertain where it touched the sea surface so that water samples could be taken in a known affected area. This task, which was carried out primarily in Plume Search Runs 1 and 2, was drastically affected by atmospheric conditions.

DIFFICULTIES ENCOUNTERED

Due to a persistent haze which created an almost white sky background at least 15° above the horizon, the plume was rarely visible from the ORCA. Even when ammonia was injected, the resulting ammonium chloride cloud often blended into the background. There were a few times, however, when it was sufficiently visible to ascertain that the plume was making contact with the sea surface.

SEA LEVEL NATURE OF THE PLUME

On those rare occasions when the ammonium chloride was observed to make contact with the ocean surface, it became apparent that the plume's movement is extremely turbulent. Thus, it does not encounter the ocean in a smooth flow. Rather it rolls over it in an erratic fashion, touching the surface in a random manner. This observation confirmed earlier impressions gained from those who reported a "now I smell it, now I don't" distribution of odor at the deck level. Part of this turbulence at sea level is probably due to wind and wave effects.

Data from Plume Search Runs 1 and 2 and Test Run II (see Figs. 1 and 2 and Tables 1 and 2) reveal that in winds of from 6 to 16 knots the overall area of plume contact with the ocean was circumscribed by a small-angle sector directly downwind of the incinerator stacks. In fact during the above three runs by ORCA when HCl was detected on deck, 80% of the times it was within a sector $\pm 10°$ of the line of wind propagation and over 95%

TABLE 1. Data on Plume Search Run I showing only the points relative to VULCANUS at which HCl odor was detected by cruise personnel on M/V ORCA. Correlate this table with Fig. 1 opposite.

Date: 3 December 1974
Position of VULCANUS: Beginning 26°49'N, 93°48'W;
End 26°55'N, 93°45'W
VULCANUS Speed and Direction: 3 knots at 030°
Wind Speed and Direction: 6-8 knots from 040°
Broken clouds

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS
1410	0.6	036°
	0.8	038°
	1.0	037°
1420	1.0	038°
	1.1	035°
1436	1.1	037°
	1.1	039°
1445	1.2	042°
	1.3	047°
1447	1.3	048°
1504	1.8	035°
	1.9	035°
1514	2.1	043°
	2.1	045°
	2.1	048°

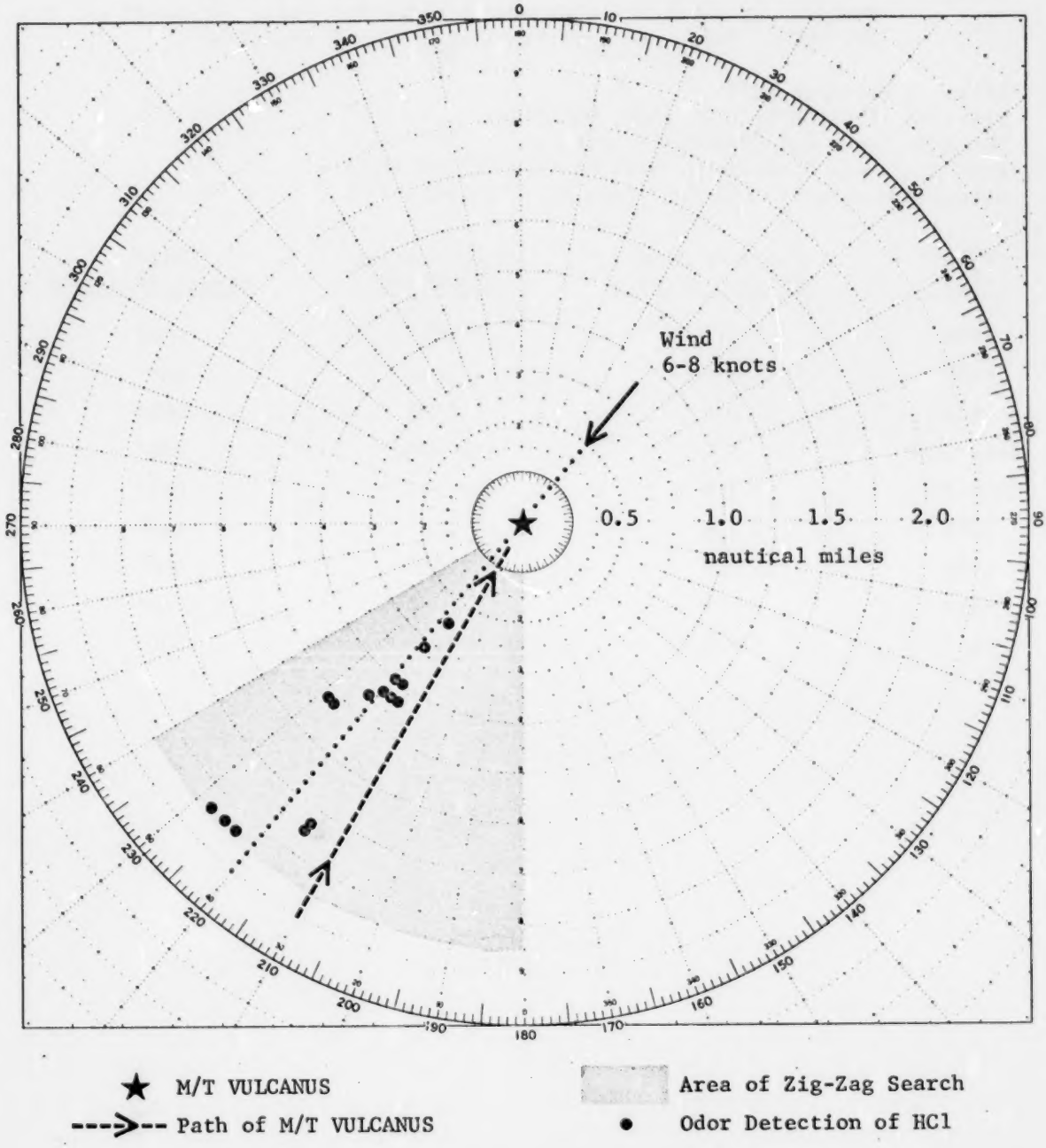
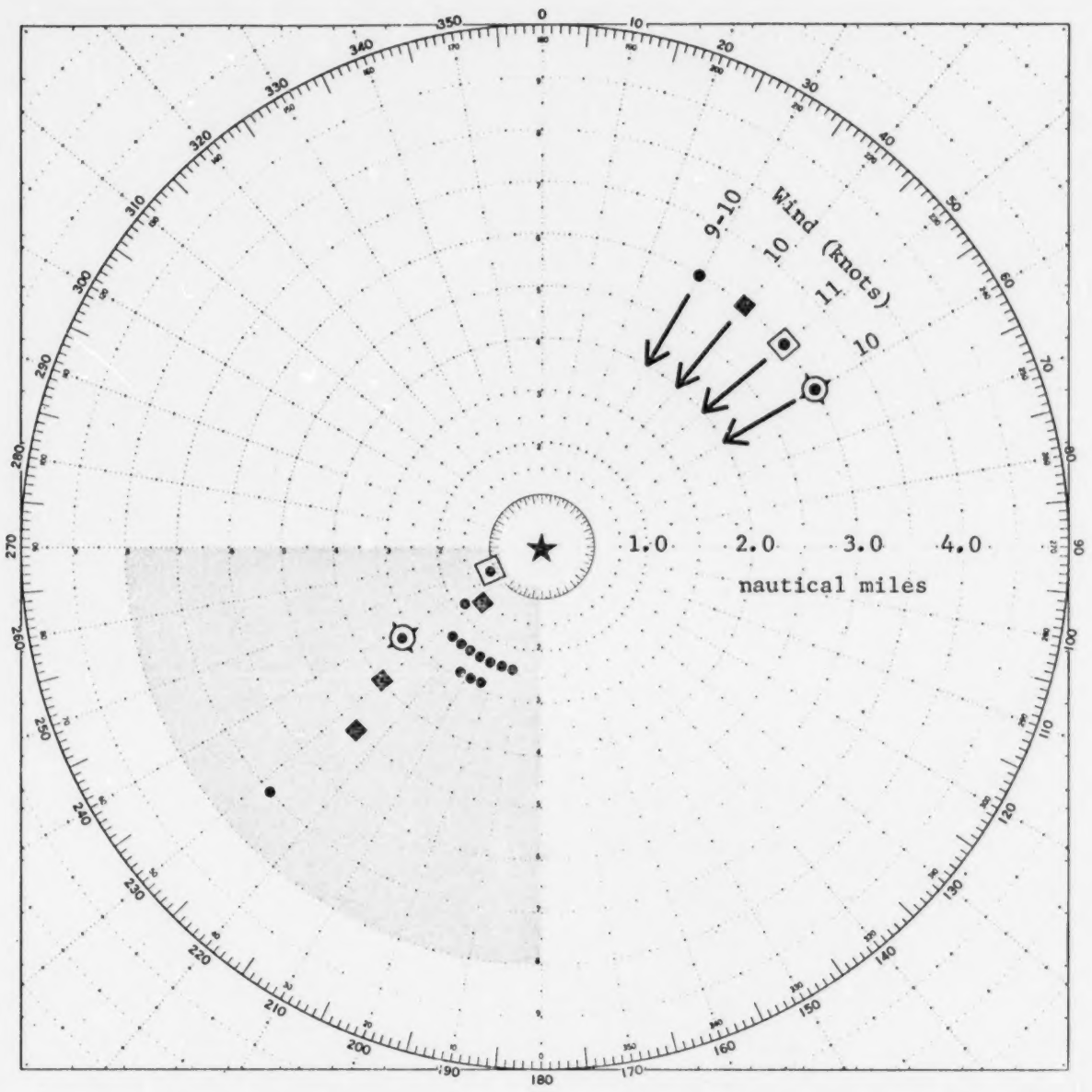


Fig. 1. Results of Plume Search Run I showing the restricted area in which HCl was detected by M/V ORCA within the sector (gray) covered by the ORCA in a zig-zag fashion. The search commenced 0.25 n.mi. behind the M/T VULCANUS and terminated about 2.2 n.mi. astern of the incinerator.

TABLE 2. Data on Plume Search Run 2 showing only the points relative to VULCANUS at which HCl odor was detected by cruise personnel on M/V ORCA. Correlate this table with Fig. 1 opposite.

Date: 3 December 1974
Position of VULCANUS: 26°55'N, 93°43'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 9-11 knots from 030°-060°
Relative Humidity: 61% (Dry Bulb 65°, Wet Bulb 57°)

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	Wind Direction (from)
1605	0.6	063°	050°
1620	0.8	043°	040°
1633	0.9	053°	030°
1642-1650	1.2	000°-044°	030°
1713-1717	1.4	024°-034°	030°
1734	1.6	057°	060°
1758	2.0	050°	040°
1829	2.5	045°	040°
1948	3.5	048°	030°



★ M/T VULCANUS (adrift)

Area of Search

● ■ ◙ ⊙ Locations at which HCl Odor was detected and Wind Direction at Time of Detection

Fig. 2. Results of Plume Search Run 2 of M/V ORCA. Note the effects of wind shifts during this run. ORCA covered the sector shown in gray from VULCANUS outward by traversing 90° arcs spaced 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 2.0, 2.5, 3.0, 3.5 and 4 n. miles from VULCANUS. This operation follows the "Plume Extent" search pattern of EPA (see Fig. 1 of Appendix A).

of the detections were made when ORCA was within ±20° of the wind line.

The major concentration of HCl detections during 6-8 knot winds was 1 to 1.25 nautical miles downwind of VULCANUS, whereas at 9-11 knots the detections were concentrated 1.25 to 1.50 nautical miles downwind.

With the above data in hand it was possible to delineate the plume with sufficient precision to permit us to carry out a meaningful program of surface water sampling.

IMMEDIATE EFFECTS OF PLUME FALLOUT

THE ANALYSIS OF THE pH VALUES

Objective

The objective of the analysis was to compare the pH values of the test runs (Test Runs I, II, and III) with the associated controls (Control Runs I and II) in order to determine whether or not the fallout HCl could override the buffering capacity of sea water and significantly depress the pH.

In order to eliminate as far as possible any biases caused by environmental differences, the following control variables were introduced into the analysis:

(i) the distance of the location of test sample from M/T VULCANUS (test runs only)

(ii) the time when the sample was collected

(iii) any possible effect of night time versus daytime sampling

More specifically (i) was introduced as a simple linear regression variable but with regard to (ii) an inspection of the data suggested that different time slopes should be introduced for the time trend during night operations as opposed to daytime operations. Both regression laws for distance and time were within experimental group trends. The analysis of variance is shown in Computation 1 as follows:

COMPUTATION 1

Analysis of Variance for pH

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F	R^2
Regression	7	0.19179	0.027399	257.5	0.973
Error	50	0.00532	0.000106		
TOTAL	57	0.19711			

The seven degrees of freedom for 'Regression' represent the amount of pH variation accounted for by differences between the 5 Runs (4 d.f.) the day and nighttime trends (2 d.f.) and the regression coefficient on the distance from the M/T VULCANUS (1 d.f.). These effects account almost completely for the pH variation as will be seen from the highly significant values of F = 257.5 and R^2 = 0.973. Indeed the experimental error mean square of 0.000106 gives us an experimental error standard deviation of $\sqrt{0.000106}$ = 0.0103 pH which is essentially identical with the pre-assessed precision of the measuring technique for pH (viz $\pm$ 0.01 pH).

For convenience of fitting the regression law the 4 degrees of freedom for contrasts in the average pH of the five Runs were represented by the following 'dummy variables'.

(i) Test Runs versus Control Runs

(ii) Test Run 3 versus Test Run 2.

(iii) Test Runs 2 and 3 versus remainder

(iv) Day Runs versus Night Runs

The regression coefficients corresponding to contrasts (i) to (iv) were then combined to obtain the contrasts of interest between Test Runs and associated Controls which are shown in Computation 2 below:

COMPUTATION 2 Estimated contrasts and their standard errors and t-ratios

Contrast	Estimate	Estimated Standard error	t-Ratio
Test 1 - Control 1	+0.02797	0.0084	3.33
Test 2 - Control 2	-0.01207	0.0069	1.75
Test 3 - Control 2	+0.02404	0.0064	3.76

TABLE 3. Results of night sampling carried out by M/V ORCA on Test Run I (see Figure opposite). Chlorinity and pH values determined by TerEco personnel; organic chloride and metal determinations by Shell Development Co. personnel.

Date: 3-4 December 1974
Position of VULCANUS: 26°50'N, 93°46'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 8-12 knots from 045°-060°

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	pH	Chlorinity (ppt)	Organic chloride (ppm)	Metals (mg/l) Cu	Zn
2223	0.25	080°	8.29	20.08			
2230	0.5	080°	8.29	20.13			
2235	1.0	080°	8.29	20.11			
2241	1.5	080°	8.29	20.08			
2246	2.0	030°	8.31	20.11			
2307	2.0	027°	8.28	20.11			
2312	1.5	025°	8.28	20.08			
2317	1.0	030°	8.29	20.13			
2322	0.5	020°	8.28	20.08			
2326	0.25	060°	8.28	20.08			
2328	0.25	060°	8.29	20.11	< .025	.006	.007
2333	0.5	060°	8.30	20.08			
2339	1.0	060°	8.29	20.08	< .025	.005	.008
2345	1.5	060°	8.28	20.06			
2350	2.0	060°	8.28	20.10	< .025	.005	.004
		Zooplankton Tow					
0029-0102	2.0-0.25	050°		Liquid	1.4	0.15	0.16
				Solid	< 3	85*	19*

* ppm

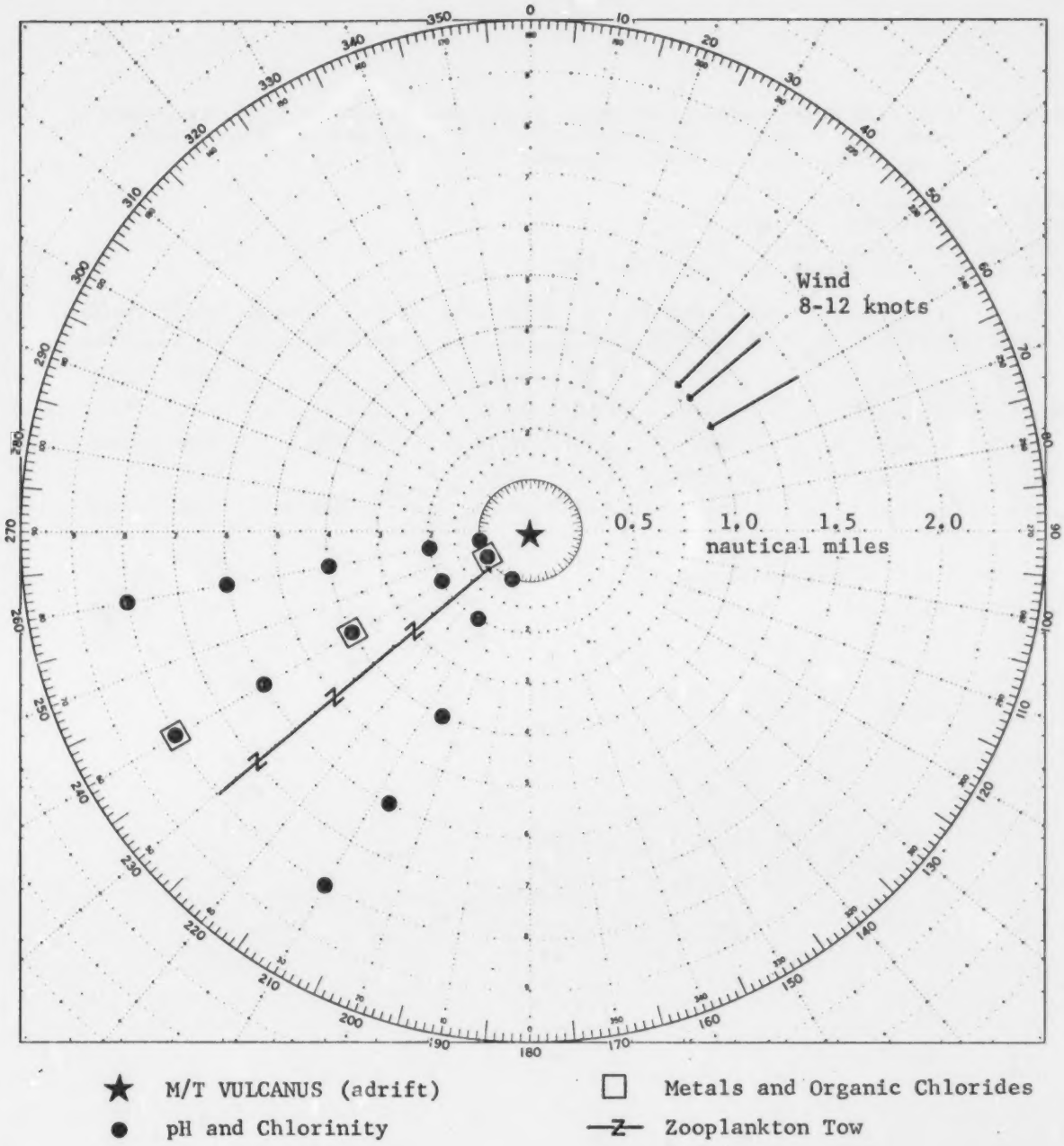


Fig. 3. Locations relative to the drifting VULCANUS of sampling stations of M/V ORCA during Test Run I. Note from Table 3 the sampling pattern followed. This operation follows the "Immediate Effects" sampling pattern of EPA (see Fig. 2 of Appendix A).

TABLE 4. Results of night sampling carried out by M/V ORCA on Control Run I (see Figure opposite). Chlorinity and pH values from TerEco; organic chloride and metal determinations made by Shell Development Co.

Date: 4 December 1974
Position of VULCANUS: 26°50'N, 93°47'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 8-10 knots from 050°

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	pH	Chlorinity (ppt)	Organic Chloride (ppm)	Metals (mg/l) Cu	Zn
0141	3.1	191°	8.26	20.01	< .025	.005	.005
0152	3.6	192°	8.26	20.12			
0203	4.1	194°	8.26	20.12	< .025	.005	.006
0215	4.6	195°	8.26	20.05			
0221	4.85	195°	8.25	20.07	< .025	.005	.004
		Zooplankton Tow					
0141-0221	3.1-4.85	191°-195°		Liquid	0.4	0.15	.05
				Solid	< 3	16*	18*

* ppm

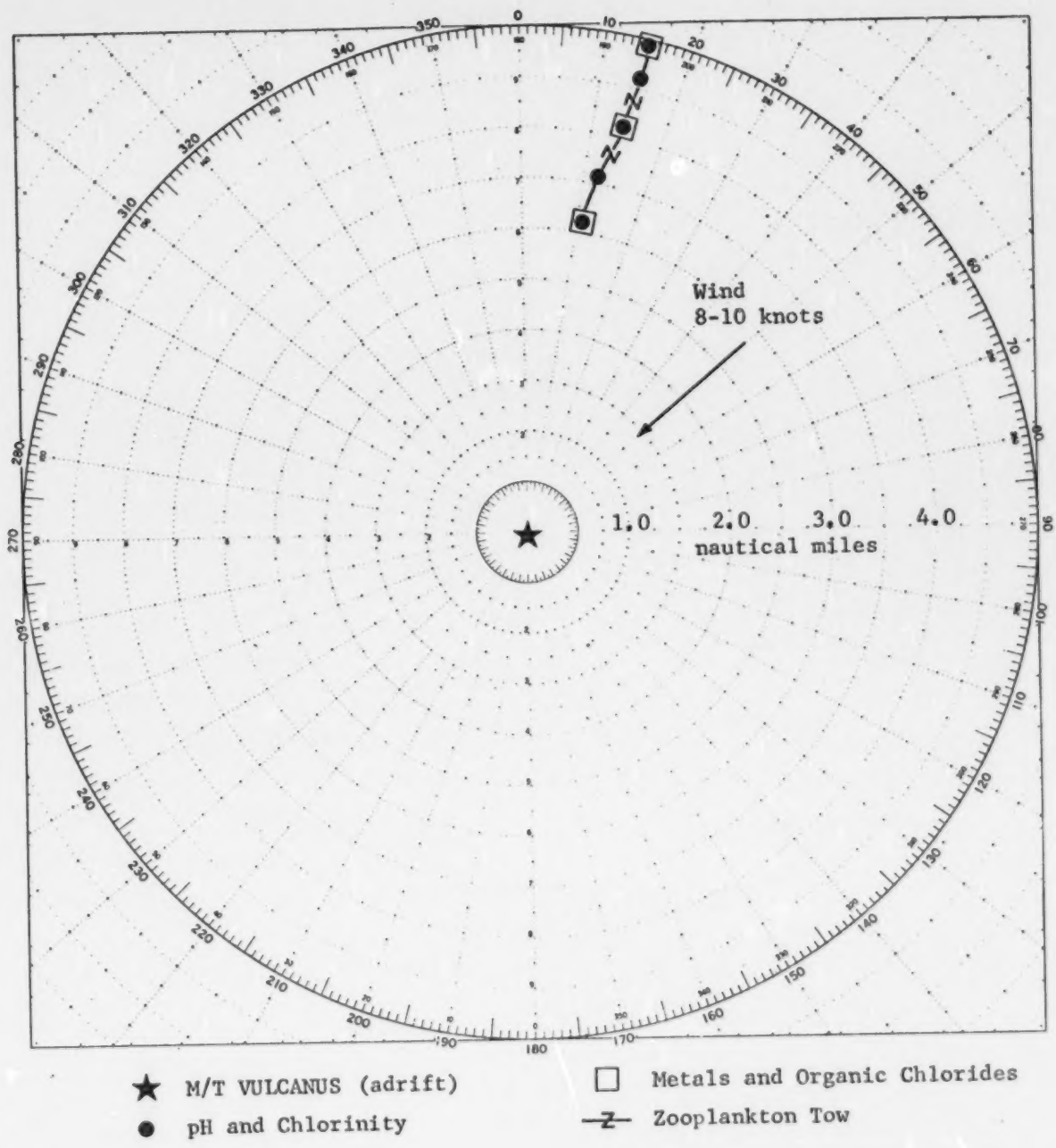


Fig. 4. Location of sampling conducted by M/V ORCA on upwind Control Run I relative to the position of drifting VULCANUS. These stations serve as the control only for Test Run I. Correlate with results in Table 4 opposite.

The only adverse effect of the incineration plume (decrease of pH) arises in Test Run 2 but this is both statistically and practically insignificant. (0.012 pH units)

The fact that Test Run 2 is the one which shows a decrease in pH was to be expected as in this Run test samples were taken at times when the incineration plume could be smelt in the air as opposed to Test Runs 1 and 3 when the sample locations were systematically distributed over the whole downwind area. The contrasts Test Run 1 minus Control Run 1 and Test Run 3 - Control Run 2 are positive. Although these contrasts are statistically significant (because of the small experimental error) they are practically insignificant (+ 0.03 and + 0.025 pH units). Although care has been taken to eliminate a bias by a time trend from these contrast estimates it should be realized that a movement to another water mass may have been easily responsible for these differences since our experimental error is by necessity a within experimental error run error. We have, however, available an interaction-error estimate. This is the single degree of freedom for the interaction between the night contrast Test 1 - Control 1 and the day contrast Test 1 & Test 3 - Control 2. The magnitude of this mean square is 0.000575 and is approximately 5.3 times larger than the within run error of 0.0001064. If the magnitude of this mean square would have been used for the computation of the t-values in Computation 2 they would have all been reduced by a factor of $1/\sqrt{5.3} = 0.435$ and would have resulted in insignificant t-values even if the degrees of freedom would have been retained at 50 (the d.f. of the experimental error). It is considered that the use of the interaction error is the valid error for inferences and that the experimental error will underestimate the true error considerably but will, of course, be most capable of pointing up any adverse effects of the incineration plume.

It is of interest to examine the magnitude of the following additional contrasts computed from the regression coefficients; they are shown in Computation 3 as follows:

COMPUTATION 3 Contrasts in pH analysis, their standard errors and t-ratios

Contrast	Regression Coefficient	St. Error	t-Ratio
Day runs v. night runs (Cont.)	0.1015	0.0140	7.25
Day runs v. night runs (Test)	0.0795	0.0082	9.67
Interaction (Day-Night) x (Test-Cont.)	-0.0220	0.0095	-2.30
Nighttime Slope	-0.00054	0.00061	-0.88
Daytime Slope	0.00099	0.00027	3.71
Regression on distance	-0.00318	0.00192	-1.66

The interpretation of the significant interaction has already been referred to. It measures the inconsistency of the Test v. Control contrast from water mass and daytime to nighttime when gauged against the within run experimental error. The surprising features are the pH Day v. Night contrasts indicating that the daytime pH values exceeded the nighttime values by about 0.10 units. Since there has not been an appreciable difference between the day- and night- temperatures it is assumed that this difference is due to one of two factors or a combination of both. In the first place there was an almost 9-hour interval of time between day and night sampling. Thus, during this time there could have been a change in current regime, bringing water into the incineration site with very different qualities. It appears advisable that t-s measurements be made in all monitoring efforts as a possible verification of such water movements. A second, and perhaps more plausible, explanation of the rise of pH in the late afternoon water samples resides with phytoplankton activity. During daylight hours these plants use free CO_2 and some extracted from bicarbonate ion in their photosynthetic activity. Two bicarbonate ions yield one carbonate ion, one molecule of CO_2, and one molecule of H_2O. The pH of the water then rises because of increased hydrolysis; but its total alkalinity does not increase, simply because one carbonate ion can't react with more hydrogen

TABLE 5. Results obtained from samples taken during Test Run II. Note that alkalinity values were determined here and in Control Run II. All parameters tested by TerEco personnel.

Date: 4 December 1974
VULCANUS Speed and Direction: 1104 to 1200 hrs - 3 knots at 090°
1200 to 1400 hrs - Adrift
when dead in water, its position was: 26°46'N, 93°39.5'W
Wind Speed and Direction: 12-14 knots from 090°
Relative Humidity: 66% (Dry Bulb 67°, Wet Bulb 60°)

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	pH	Chlorinity (ppt)	Alkalinity (meq $[H^+]$/l)
1112	0.5	100°	8.37	20.05	2.54
1139	3.0	097°	8.37	20.12	2.48
1141	3.1	101°	8.37	20.07	2.50
1213	4.3	107°	8.36	20.07	2.48
1214	4.2	103°	8.36	20.10	2.56
1308	3.0	087°	8.35	20.07	2.51
1309	2.8	088°	8.35	20.10	2.54
1311	2.8	095°	8.36	20.19	2.50
1314	2.8	105°	8.37	20.12	2.52
1325	2.5	092°	8.37	20.05	2.53
1326	2.5	090°	8.37	20.10	2.50
1328	2.6	086°	8.37	20.10	2.52
1331	2.4	082°	8.37	20.03	2.52
1333	2.0	091°	8.37	20.03	2.50
1345	1.5	090°	8.36	19.94	2.54
1351	1.1	088°	8.37	20.14	2.48
1352	1.1	091°	8.37	20.10	2.46
1357	0.5	094°	8.37	20.07	2.46

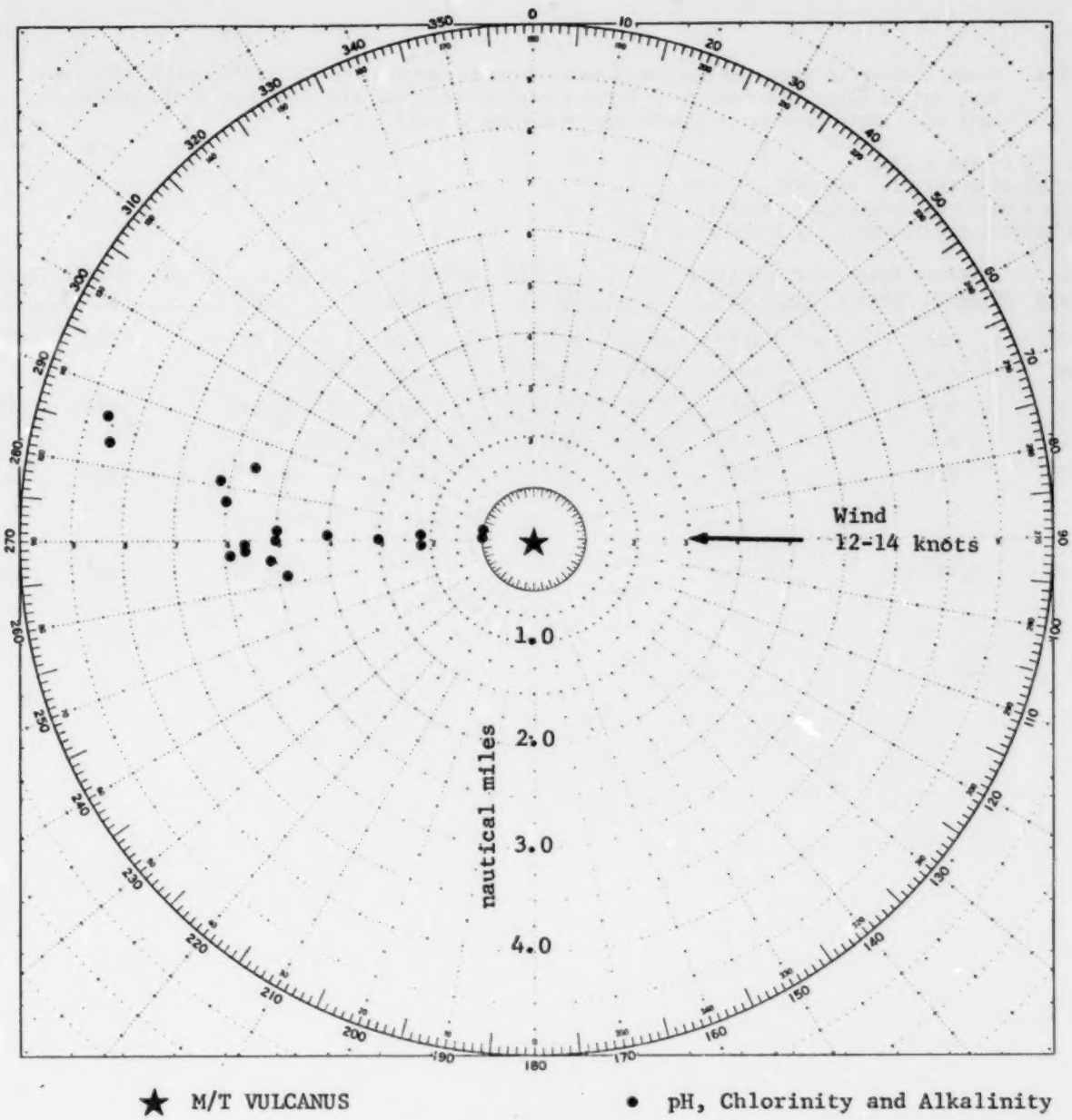


Fig. 5. Locations of water samples taken during Test Run II only when personnel on M/V ORCA detected HCl in the air. ORCA followed a zig-zag course while moving away from and back toward VULCANUS, which was drifting during most of the sampling (see Table 5 opposite).

TABLE 6. Results obtained from samples taken during upwind Control Run II. Alkalinity, chlorinity, and pH values determined by TerEco; organic chloride and metals by Shell Development Co. These data are controls for Test Runs II and III.

Date: 4 December 1974
Position of VULCANUS: 26°45'N, 93°42'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 12 knots from 090°

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	pH	Chlorinity (ppt)	Alkalinity (meq $[H^+]$/l)	Organic Chloride (ppm)	Metals (mg/l) Cu	Zn
1447	3.9	202°	8.39	20.12	2.48	<.025	.004	.004
1459	4.4	203°	8.39	20.12	2.46			
1510	4.9	204°	8.39	19.97	2.46	<.025	.003	.004
1520	5.4	206°	8.39	20.00	2.46			
1527	5.65	206°	8.39	19.95	2.46	<.025	.004	.004
		Phytoplankton Tow						
1447-1527	3.9-5.65	202°-206°				< 3	.030	.080

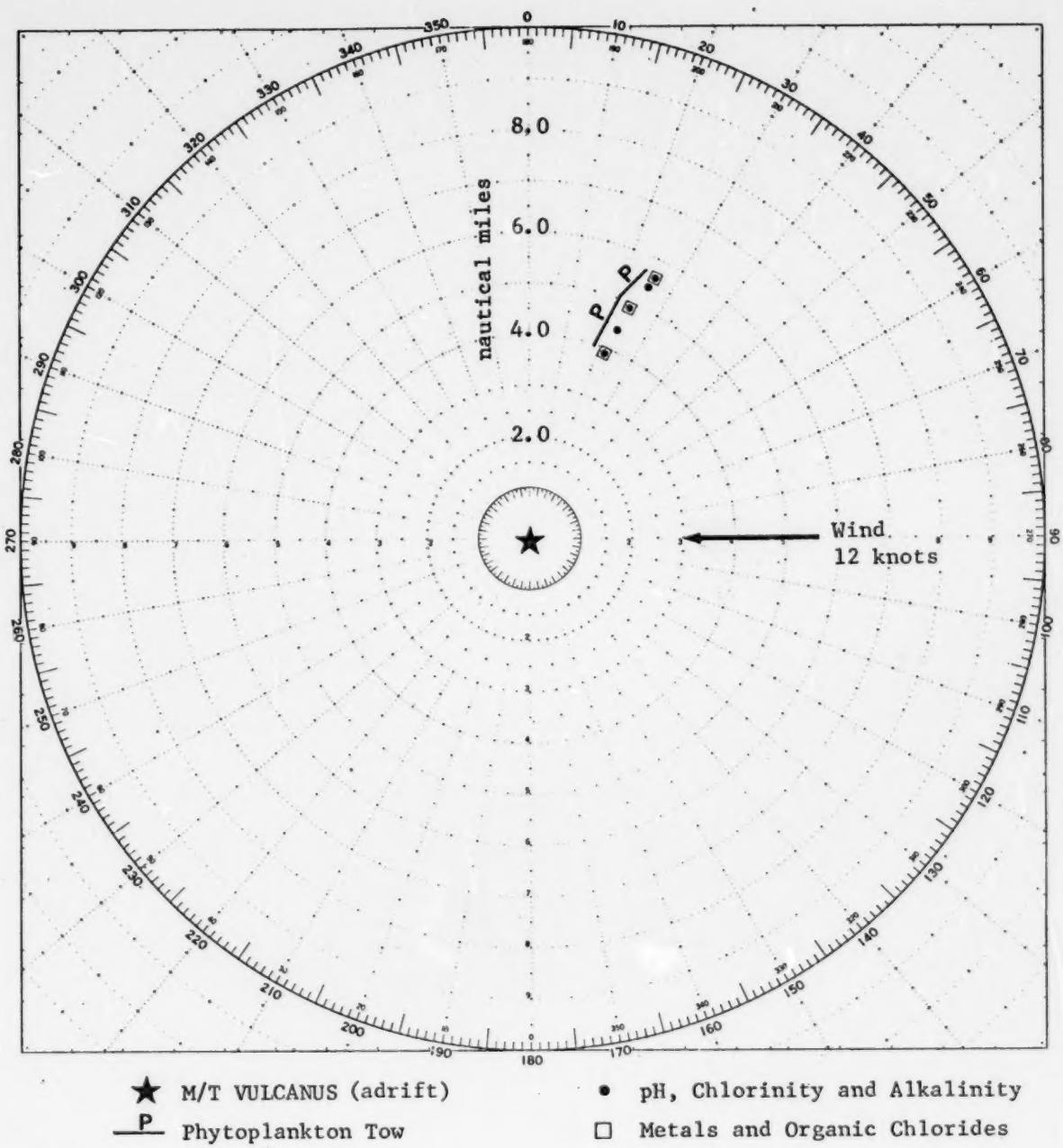


Fig. 6. Location of stations taken by M/V ORCA during upwind Control Run II relative to drifting VULCANUS. This run is the control for both Test Runs II and III. For results see Table 6 opposite.

ions than can two bicarbonate ions. The process is reversed at night, photosynthesis ceases then but respiration of both plants and animals goes on. Hence the increase in CO_2 concentration results in decrease of pH.

THE ANALYSIS OF THE CHLORINITY MEASUREMENTS

The analysis of these records is analogous to that of the pH values described in the preceding section. The analysis of variance is shown in Computation 4.

COMPUTATION 4. Analysis of Variance for Chlorinity

Sources of Variation	Degrees of freedom	Sum of Squares	Mean Square	F	R^2
Regression	7	0.18615	0.026593	13.5	0.654
Error	50	0.09867	0.001973		
TOTAL	57	0.28483			

The regression as a whole is again significant but the R^2 value of 0.654 is lower than in Computation 1. The experimental error standard deviation is $\sqrt{0.001973} = 0.0444$ just in excess of the assessment of the error in the measuring techniques for chlorinity which was $\pm$ 0.03 units. However of the contrasts contributing to the regression is a negative daytime trend of -0.0040 per test interval corresponding to the upward trend in pH of 0.00099 per test interval. We confine ourselves to setting out the contrasts between Test Runs and associated Control Runs as shown in Computation 5 below:

COMPUTATION 5. Estimated Contrasts and Their Standard Errors in t-Ratios

Contrast	Estimate	Estimated Standard Error	t-Ratio
Test 1 - Control 1	0.0064	0.0361	0.177
Test 2 - Control 2	0.0166	0.0297	0.557
Test 3 - Control 2	-0.0309	0.0276	-1.123

TABLE 7. Results of day sampling carried out by M/V ORCA on Test Run III (see Figure opposite). Chlorinity and pH values determined by TerEco personnel; organic chloride and metal determinations by Shell Development Co. personnel.

Date: 4 December 1974
Position of VULCANUS: 26°44'N, 93°43'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 12-15 knots from 090°

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	pH	Chlorinity (ppt)	Organic Chloride (ppm)	Metals (mg/l) Cu	Zn
1630	0.2	103°	8.44	20.02			
1634	0.5	102°	8.43	19.98			
1637	1.0	102°	8.44	20.01			
1641	1.5	102°	8.44	19.96			
1645	2.0	104°	8.43	19.95			
1652	2.0	080°	8.42	19.90			
1655	1.5	077°	8.42	19.99			
1658	1.0	076°	8.41	20.02			
1702	0.5	076°	8.42	19.94			
1703	0.25	070°	8.42	19.94			
1715	0.25	113°	8.41	19.99	<.025	.006	.005
1721	0.5	093°	8.42	19.92			
1733	1.0	092°	8.42	19.90	<.025	.005	.007
1745	1.5	097°	8.42	19.94			
1751	2.0	092°	8.42	19.94	<.025	.006	.005
		Phytoplankton Tow					
1721-1751	0.25-2.0	113°-92°			< 3	.036	.09

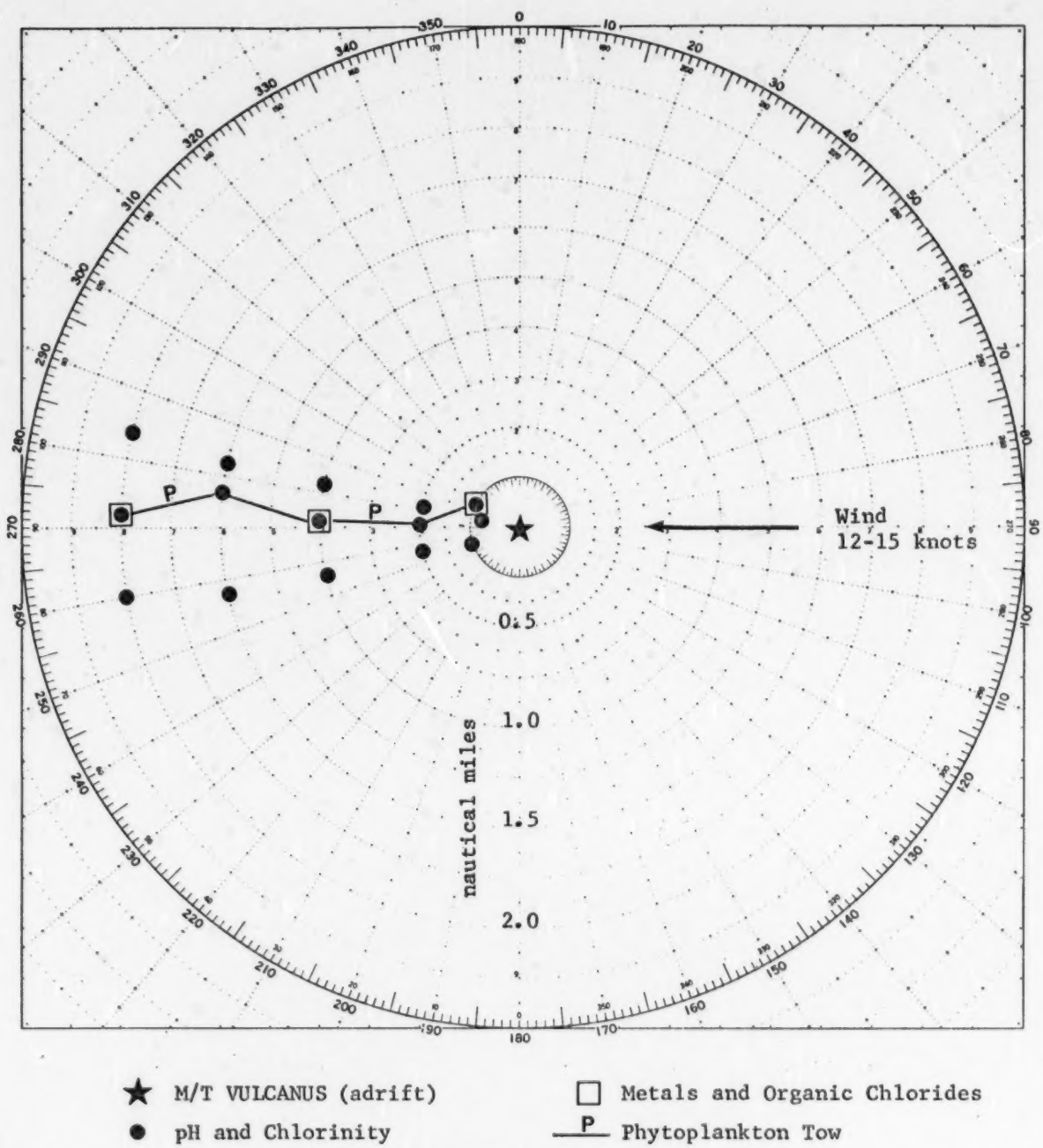


Fig. 7. Locations relative to the drifting VULCANUS of sampling stations of M/V ORCA during Test Run III. Note from positions in Table 7 the sampling pattern followed. This operation follows the "Immediate Effects" sampling pattern of EPA (see Fig. 2 of Appendix A).

The difference between Test 1 and Control 1 is quite insignificant, and that between Test 2 and Control 2 is larger but the difference is again insignificant. The difference between Test 3 and Control 2 is in a direction in which chloride would be reduced (!) through the incineration plume. However, this difference is again quite insignificant. All contrasts are therefore chance effects explainable by the experimental error.

THE ANALYSIS OF THE ALKALINITY MEASURES

These chemical determinations are only available from the samples taken in Test Run 2 and Control Run 2. Accordingly the Analysis of Variance is based on fewer observations as shown in Computation 6.

COMPUTATION 6 Analysis of Variance for Alkalinities (All records multiplied by 100)

Sources of Variation	Degrees of freedom	Sum of Squares	Mean Square	F	R^2
Regression	3	94.127	31.38	4.84	0.433
Error	19	123.177	6.48		
TOTAL	22	217.304			

Both the F-ratio for regression and the R^2 value are barely significant indicating that the regression is not too well confirmed. The experimental error standard deviation is $\sqrt{6.48} = 2.55$ units in the 2nd decimal of the alkaline records. This is 2 1/2 times the error in the measurement technique indicating more environmental differences within a run. None of the effects are significant. Specifically the contrast for treatment minus control is + 0.019 with a standard error of 0.020.

THE ANALYSIS OF ORGANIC CHLORIDE MEASUREMENTS

In Water

A limited number of water and plankton samples were analyzed for organic chloride (see Tables 3, 4, 6, 7, 8 and 9). Actually a total of

TABLE 8. Organic chloride and metal determinations derived from 1-hour zooplankton sample of Test Run IV. Determinations made by Shell Development Co.

Date: 4 December 1974
Position of VULCANUS: 26°43'N, 93°47'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 16 knots from 110°

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	Organic Chloride (ppm)		Metals (mg/l) Cu	Zn
2228	1.7	108°				
2250	0.9	106°				
2257	0.4	100°				
2258	0.4	093°				
2308	0.8	107°				
2331	1.6	115°				
			Liquid	0.2	0.67	0.20
			Solid	< 3	6*	13*

* ppm

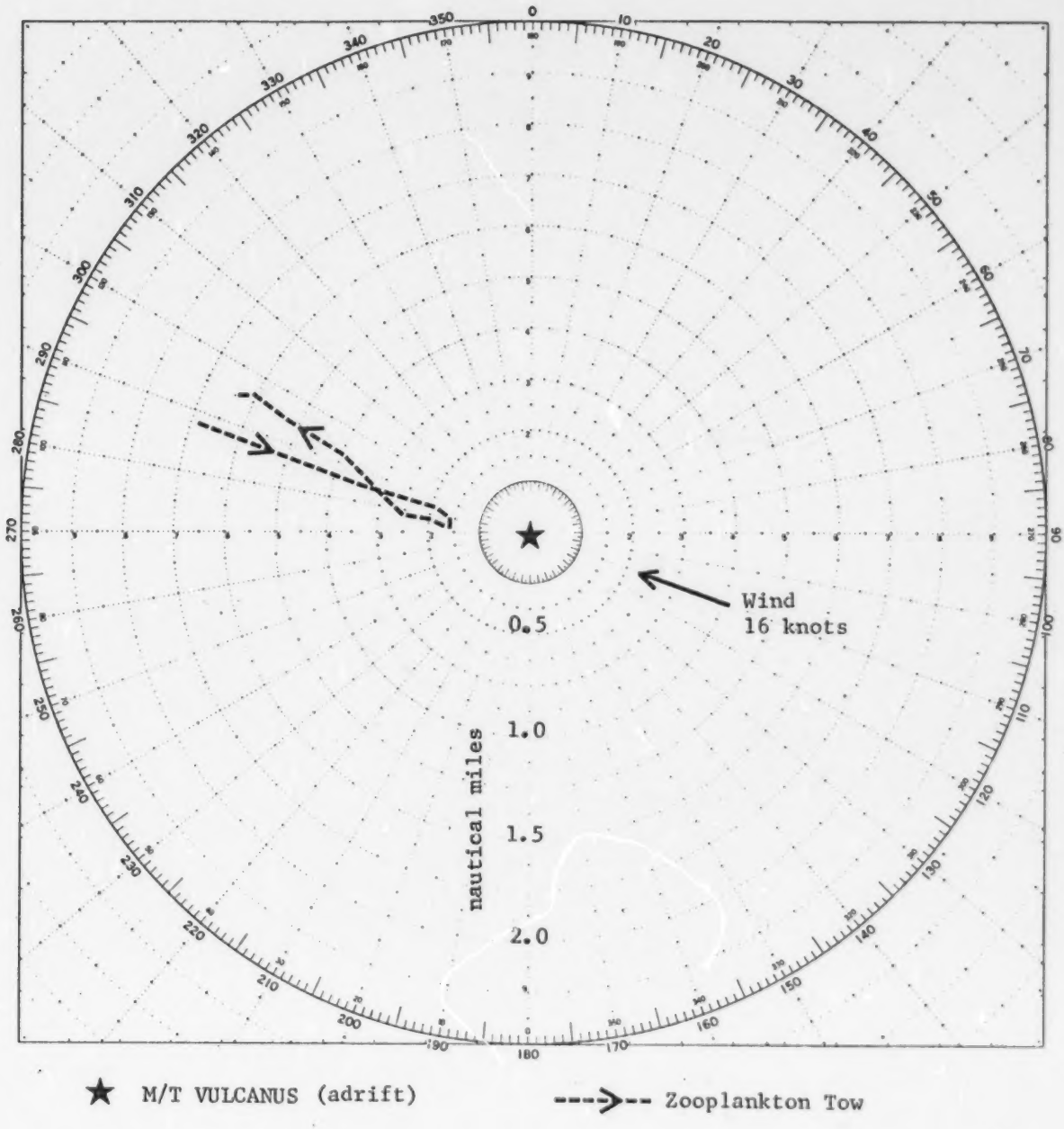


Fig. 8. Path of Test Run IV 1-hour zooplankton tow of M/V ORCA relative to the drifting VULCANUS. This operation follows the "Long Range Effects" sampling pattern of EPA (see Fig. 3 of Appendix A).

12 water samples per se was examined for the presence of organic chlorides. There was absolutely no detectable difference among these samples, since all of them measured below the level of chemical detectibility, viz., less than 0.025 ppm.

In Plankton

See below under Long Range Effects.

THE ANALYSIS OF COPPER AND ZINC MEASUREMENTS

In Water

A total of 12 water samples were also analyzed for concentrations of copper and zinc (see Tables 3, 4, 6, and 7). We can detect no significant differences between the Test and Control samples. If this activity is to be included in any future monitoring projects, it would be advisable to increase the number of samples taken to reach a point appropriate for rigorous statistical analysis.

In Plankton

See below under Long Range Effects.

LONG RANGE EFFECTS

Three different analyses were carried out to gain some insights into possible long-range effects of organic and metallic components of plume fallout. These were ascertained by a series of lengthy tows for zooplankton (Tables 3, 4, 8, and 9) and for phytoplankton (Tables 6 and 7) and their subsequent chemical analysis for organic chlorides and copper and zinc.

ORGANIC CHLORIDES

Zooplankton.- The distribution of organic chlorides was determined both in the liquid phase and the organismic phase. No detectable difference was found in the concentration of organic chlorides between test and control organisms--all were less than 3 ppm, which is the limit of determination in the sample sizes provided. On the other hand, the concentrations of organic

TABLE 9. Organic chloride and metal determinations derived from M/V ORCA 1-hour zooplankton sample of Control Run III. Determinations made by Shell Development Co.

Date: 5 December 1974
Position of VULCANUS: 26°44'N, 93°49'W
VULCANUS Speed and Direction: Adrift
Wind Speed and Direction: 16 knots from 110°

Time (local)	Distance from VULCANUS (n.mi.)	True Bearing to VULCANUS	Organic Chloride (ppm)	Metals (mg/l) Cu	Zn
0010	3.1	212°			
0026	3.7	216°			
0039	4.2	221°			
0051	4.8	221°			
0054	4.8	222°			
0102	4.3	226°			
0110	4.0	227°			
		Liquid	2.0	0.93	0.04
		Solid	< 3	11*	28*

* ppm

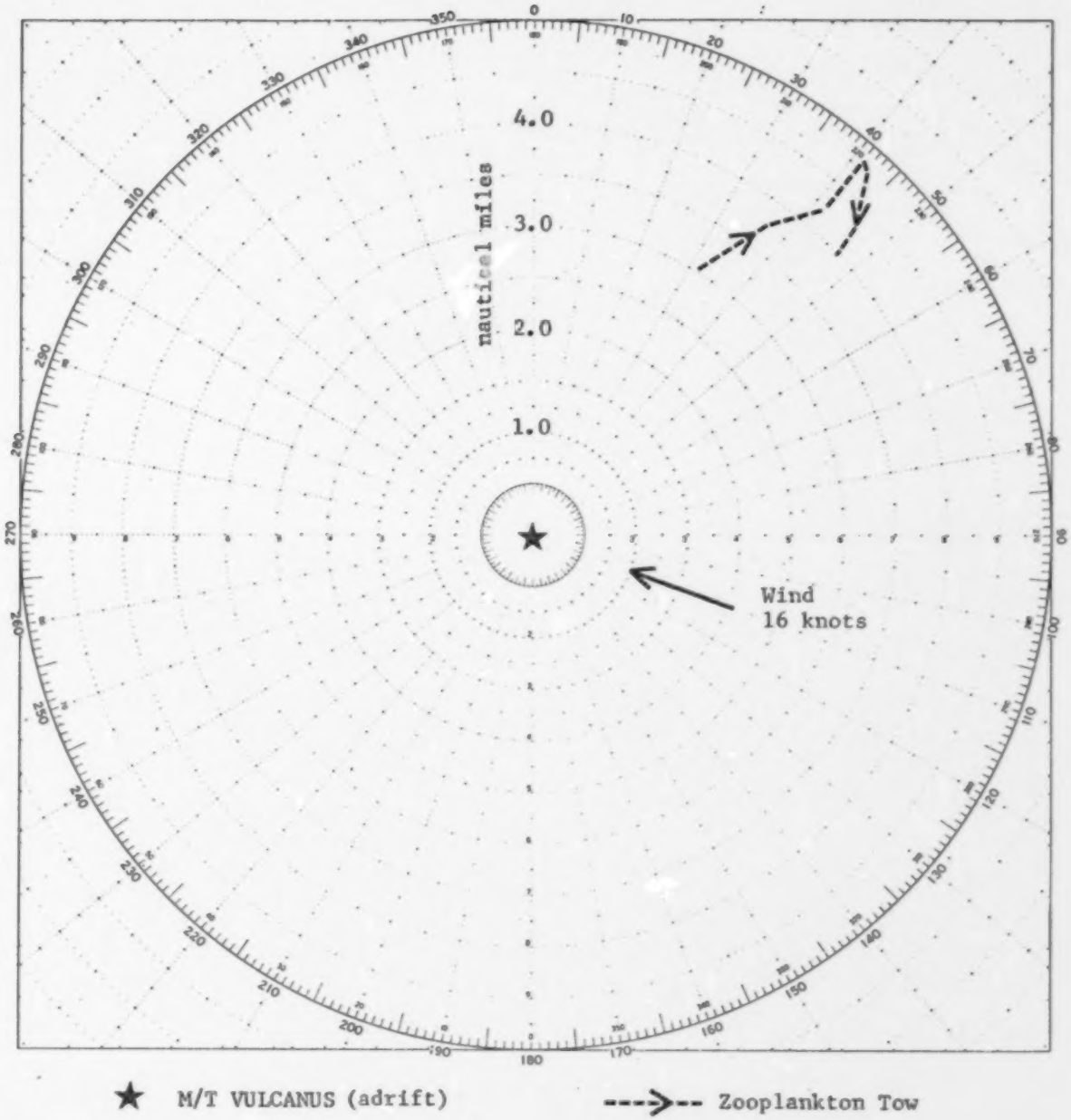


Fig. 9. Path of upwind Control Run III 1-hour zooplankton tow of M/V ORCA. This run serves as the control only for Test Run IV (see Fig. 8).

chlorides in the liquid phases varied from 0.2 to 2.0 ppm. It is felt, however, that these levels and differences are not attributable to plume fallout. In the first place, the level in Test Run I sample was 1.4 ppm with a control level (Control Run 1) of 0.4 ppm, whereas in Test Run IV the level was 0.2 ppm with a control level (Control Run III) of 2.0 ppm. Secondly, it seems likely that the high levels in some liquid phase samples is due to varying amounts of tar ball materials in the samples. As was mentioned earlier in the Methods section of this report, attempts were made to avoid contaminating the plankton samples with floating oil and plastics, but this was not completely successful. The relevance of this to an explanation of the high value of organic chlorides in some liquid phases was pointed up by the following observation:

The Shell Production Co. personnel ran an analysis of some tar materials found in the liquid phase of the zooplankton sample and found them to run unexpectedly high in organic chlorides. This appears to be worthy of further investigation on a much larger scale.

A final point should be made in regard to the organic chlorides found in these samples, viz., for the most part the compounds found had higher molecular weights than those in the Shell wastes.

Phytoplankton.- The phytoplankton materials (2 tows only) show no difference between test and control runs, the concentrations being something less than the detectibility limit of 3 ppm.

COPPER AND ZINC

The metal analyses reveal nothing to indicate with certainty that the plume fallout has caused any appreciable increases of copper and zinc in either the water or the organisms. For instance, the highest value for Cu in liquid, 0.93 mg/l, was found in the liquid phase of the Control Run III for zooplankton (Table 9), whereas the lowest values, 0.030 and 0.036 were found in the phytoplankton (liquid and organism) samples from the control and test tow, respectively (Tables 6 and 7).

Zinc values tended to be more conservative, but again the results were mixed with some values being higher in the controls than in the test runs.

SUGGESTED MONITORING ACTIVITIES

During preparation of this report, TerEco personnel have identified certain activities that they believe will enhance the circumspection of any future monitoring program related to incineration of organic wastes at sea. These will only be touched upon briefly in this report.

LONG RANGE EFFECTS

This aspect of the program can be strengthened considerably by use of a device for enclosing a discrete parcel of water and its contained biota in such manner that its identity can be maintained for periods of several days. The enclosure would not be fabricated of plastic. Rather it would take the form of a large cylinder (e.g. 2 X 5 m) made of phytoplankton size mesh, i.e., between 35-60 microns. These cylinders would be supported by flotation rings and counter-weighted to hold them taut while floating. Equipped with radar screens, they would be deployed in both Test and Control runs and permitted to drift with the impacted or unaffected waters. After a suitable length of time (perhaps several days--depending on sea conditions) they would be retrieved. Appropriate tests could then be run on the contained biota and meaningful comparisons between Test and Control samples could then be made.

IMMEDIATE EFFECTS

IN WATER

Alkalinity

It is recommended that alkalinity measurements be added to the protocol. Using a potentiometric titration and the differential method of calculation, this is a very sensitive approach to determinations of small changes in the buffering capacity of sea water.

pH

It is suggested that the value of monitoring for pH change could be enhanced considerably by use of an automated system mounted on the

ship's forward deck. Briefly, this system would provide a continuous read out of pH in

(1) thin films of distilled water

(2) filtered sea water, and

(3) ambient sea water being pumped from surface water near the ship's bow.

These measurements would be recorded, with a time marker, on a 4-channel recorder. This system is relatively simple and inexpensive (a design layout is available) but it would give much information on

(1) very immediate presence of HCl at deck level (change in distilled H_2O),

(2) the influence of organisms on changes in water (comparison between filtered and ambient water), and

(3) could provide insights into the problem of night vs. day changes previously observed.

T-S Structures

During preparation of this report the desirability of having some means of detecting major changes in ambient water masses became quite evident. It is suggested, therefore, that STD measurements be made on a regular basis during each sampling run.

IN AIR

In our judgment the capability of monitoring the air column should be provided on the monitoring ship. Recognizing that aircraft flights are expensive and can only be made periodically (and perhaps not at all if weather conditions are not favorable), it is suggested that the monitoring vessel be provided with a balloon (stream-lined) of sufficient size to lift a 100 lb payload. This inflatable (helium) would be tethered to a suitable winch by means of conducting cable. Thus, it could be run up and down at will in order to carry gas-sampling bags to appropriate

elevations for plume ascertainment. Again, it is not appropriate to go into detail here as to the devices that it would carry aloft. Suffice it to say that it would have a recording aneroid for marking altitude, and the bag rack would be arranged so that air samples could be pumped on command from the deck and released for cable fall to the deck ad seriatum.

The above are not intended to represent the entire protocol of a monitoring program.

SUMMARY-CONCLUSIONS

Based upon the findings of the sea-level monitoring program carried out by TerEco Corporation personnel aboard M/V ORCA, it is concluded that the burning of the organic chloride wastes derived from the Shell Deer Park Complex by M/T VULCANUS caused no detectable changes in the waters of the Gulf of Mexico that would be harmful to the marine biota.

This conclusion is based upon the facts that

1. We found no significant differences between the pH and chlorinity values of the Test and associated Control runs, even though
2. The tests were sufficiently discriminatory as to (a) delineate differences in sampling techniques (selective vs. random sampling) and (b) to detect differences in day and night CO_2 content of the waters.

It is suggested that the technique for determination of possible long-range effects can be improved in future monitoring programs.

Nevertheless, on balance it is concluded that incineration at sea is the most effective method now available for the relatively harmless disposal of organic chloride and related wastes.

APPENDIX A

November 22, 1974

MARINE ENVIRONMENTAL MONITORING

I. Background

The organic chloride wastes are to be burned completely with the evolution of HCl and CO2, which are then to be exhausted through the incineration stack without further treatment. There are four aspects of the impact of the incinerated wastes on the environment:

1. HCl is exhausted from the stack in large quantities and will either be dispersed in the air over a large area or will be dissolved in the ocean water where the stack emissions reach the ocean surface.
2. Some organic chlorides may not be destroyed during the incineration and may enter the marine environment similarly to the HCl.
3. Trace metals in the waste will not be destroyed during the incineration and may enter the marine environment through the same mechanisms as the HCl.
4. Both organic chlorides and trace metals may enter the food chain and be bioaccumulated, with potentially adverse effects on the marine ecosystem.

The previous monitoring operations were designed to obtain data to identify problems assocciated with all of these aspects insofar as surface measurements could be expected to reflect the potential for any problems. The operations included the following types of measurements:

1. Plume identification. An essential part of detecting any environmental impact is to determine where the plume, if any, touches the surface of the ocean. Only at the air-sea interface where any

plume constituents are being dissolved into the ocean will the concentrations be expected to be high enough to show clearly detectable transient impacts such as pH changes.

2. Sampling for immediate impact in the area directly affected by the plume.
3. Sampling for overall impact in the general area affected by the burn.

A two phase program was set up, first an exploratory cruise at the beginning of the burn in which major emphasis was placed on plume identification techniques and sampling for immediate impacts; and, second, a cruise at the end of the burn in which emphasis was placed on sampling the water under the plume to detect immediate impacts and sampling systematically a large area impacted during the burn to detect any long-range impacts.

The parameters by which immediate impacts on the ocean were measured were pH, Chlorides, Organic chlorides, and Trace metals. Parameters by which long-range impacts were measured were the parameters listed above plus indicators of damage to marine life such as changes in phytoplankton counts, chlorophyll-a, and ATP.

The conclusions reached after these cruises, insofar as marine environmental monitoring operations are concerned, are as follows:

1. The plume can be identified with suitable sampling equipment and its location established in relation to VULCANUS.
2. The location of the plume as a function of wind speed and direction can be predicted with sufficient accuracy to set up an effective search pattern to find it easily.

3. There was some indication that there might be identifiable immediate impacts in terms of pH and Chlorinity changes where the plume touches the ocean surface; but any such impacts, if they are real, are extremely transient.
4. Organohalogen impacts on water chemistry and alternations in trace metal concentrations were undetectable and are likely to be so except possibly during rainstorms where any plume contaminants would be scrubbed from the air in the near vicinity of VULCANUS.
5. The amount of marine life in the incineration site is so small that levels of chlorophyll-a, ATP, and primary productivity are so small that any changes due to impacts are likely to be obscured by analytical or sampling variations.

Based on the results and conclusions outlined above, a new operational plan was developed to improve the surface monitoring operations by eliminating unproductive sampling. The approach, however, still consists of the three major components of plume identification, immediate effects determination, and long range effects determination.

II. Operational Plan

A. Plume Identification

Plume identification will be made with the same type of HCl monitor that was used on the previous cruises. This instrument works well on shipboard except during rain and when exposed to salt water spray. It has high sensitivity and provides a continuous real-time readout of HCl concentrations in the air. This instrument will be operated continuously while sampling and

a running log of position relative to VULCANUS and HCl air concentration will be kept.

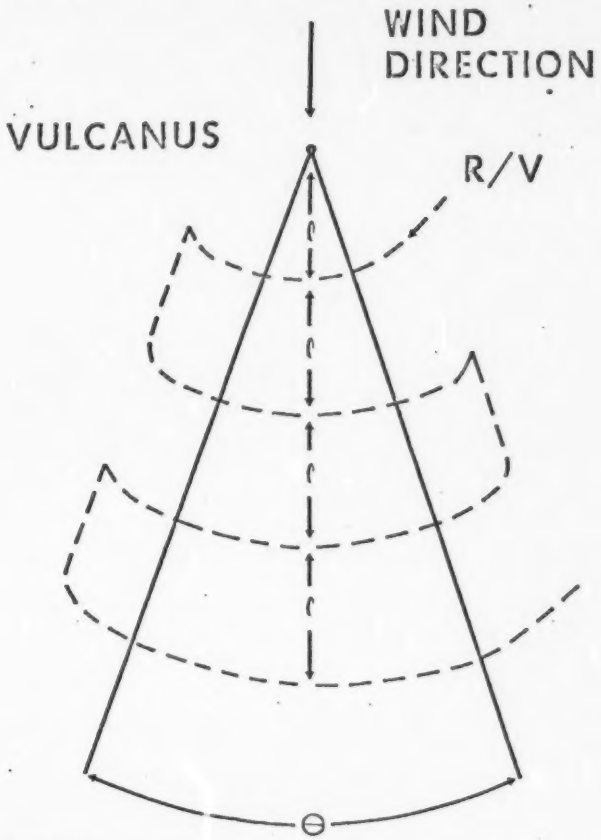
The basic pattern to be used for finding the plume and mapping its extent is shown in Figure 1. The approach is to sweep an arc downwind of VULCANUS at distances within which the plume is likely to be found. The distances and sweep angles used have been estimated from the observations made by OREGON II during the first burn. The distances from VULCANUS and spacing of the arcs is keyed to the wind speed during the run. The fundamental assumption is that the wind speed and direction will remain relatively constant during a run; this is a reasonable assumption for all but stormy weather when sampling may not be possible, or in calm weather when VULCANUS will have to maneuver to maintain 10 knots windspeed across the incinerator stacks.

The monitoring vessel will make its first run at the distance shown in Figure 1 and then will sweep back across the sector at twice this distance. This procedure will continue until the point of plume touchdown has been passed and HCl readings are down to background all along the last arc swept. If the plume is not identified within ten sweeps of the search sector, the search will be terminated, and a new search pattern initiated using greater incremental distances (l) and wider sweep angles (Θ) from VULCANUS, but not extending more than 10 miles from VULCANUS or greater than 180 degrees total angle.

If use of the search patterns outlined above does not locate the plume it is unlikely that the plume touches the ocean surface in concentrations high enough to detect an impact. The plume may be visible if the humidity is

FIGURE 1

PLUME EXTENT SEARCH PATTERN



WIND SPEED (KNOTS)	r (N. M.)	Θ** DEGREES
<10*	--	--
10	.04	90
15	.10	90
20	.25	60
25	.50	45
>25	.50	45

Θ=SWEEP ANGLE

r=DISTANCE BETWEEN TRANSECTS

*VULCANUS REQUIRED TO MAINTAIN WINDSPEED OF 10 KNOTS OVER INCINERATORS

**ASSUMING STEADY WIND DIRECTION. IF WIND DIRECTION VARIES, ADD VARIATION IN WIND DIRECTION OVER 30 MINUTES TO Θ TO OBTAIN SWEEP ANGLE

high and the ambient temperature low. If such is the case the plume extent can be identified visually and its extent confirmed by use of the HCl monitor.

During rainy conditions, the plume may not exist more than a few hundred meters from the ship, and tracking the plume with the HCl monitor may not be feasible. Under such conditions, however, any immediate impacts on the marine environment should occur in the immediate vicinity of the ship and the water sampling will be planned on this assumption.

B. Sampling For Immediate Effects

Once the plume is identified, samples to identify any immediate effects will be taken. Figure 2 shows the sampling grid to be occupied and the types of samples to be taken at the various stations. All samples will be surface samples which can be taken by bucket.

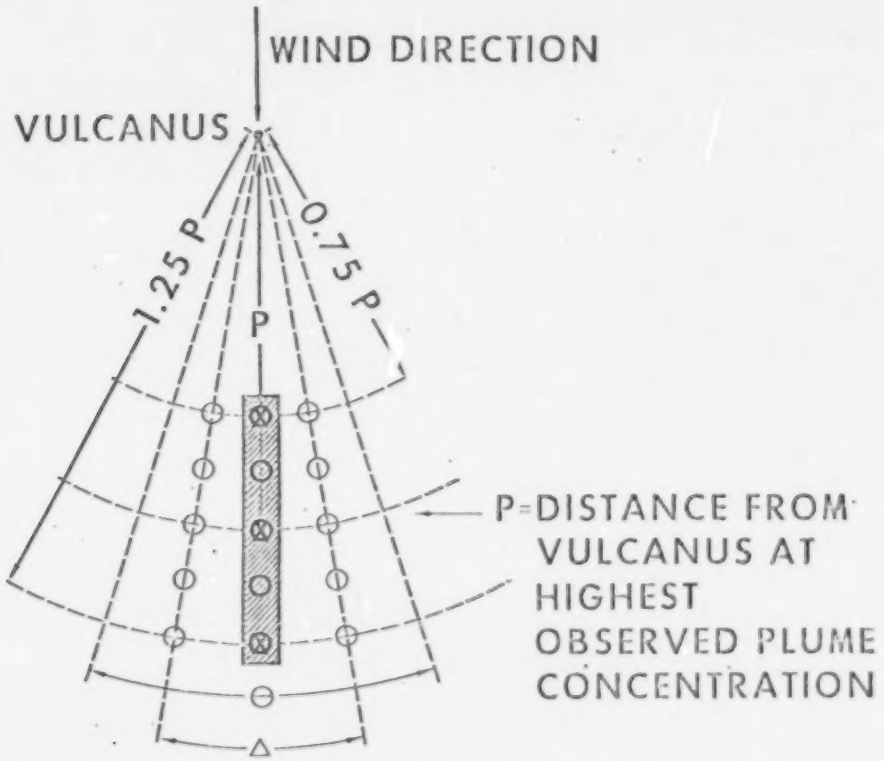
The primary parameters are pH and Chlorides. The pH samples will be run immediately and the Chloride samples will be titrated on shore. Chloride samples will be stored in clean, dry, distilled-water-rinsed, glass bottles without addition of any preservatives. A total of 15 such samples will be taken.

Three samples will be taken in the center of the grid for organohalogens and trace metals. Organohalogen samples will be placed in acetone-washed glass bottles with Teflon or Aluminum foil lids for on-shore analysis. Trace metal samples will be placed in plastiic bottles and preserved with nitric acid for on-shore analysis.

In addition to these samples a plankton tow will be made through the center of the impact area, for phytoplankton in the daytime, and

FIGURE 2

IMMEDIATE EFFECTS SAMPLING PATTERN



△ DISTANCE OVER WHICH READINGS WERE FOUND

Θ SWEEP ANGLE

O SAMPLING STATIONS FOR pH AND CHLORINITY

▨ PLANKTON TOW

DAY PHYTOPLANKTON
NIGHT ZOOPLANKTON

× SAMPLING STATIONS FOR TRACE METALS AND ORGANOHALOGENS

for zooplankton if the run is made at night. These samples will be preserved for analysis for organohalogens and trace metals.

C. Sampling for Long Range Effects

Long range effects will show up in the impact of the incinerator emissions on marine biota. The only index by which these could be measured, with the low productivity of the dumpsite, will be through collection and analysis of the indigenous biota. Figure 3 shows the procedures to be used. While the VULCANUS is drifting for one hour, continuous tows for both phytoplankton and zooplankton will be taken in the impact area of the plume. These samples will be preserved for analysis for organohalogens and trace metals.

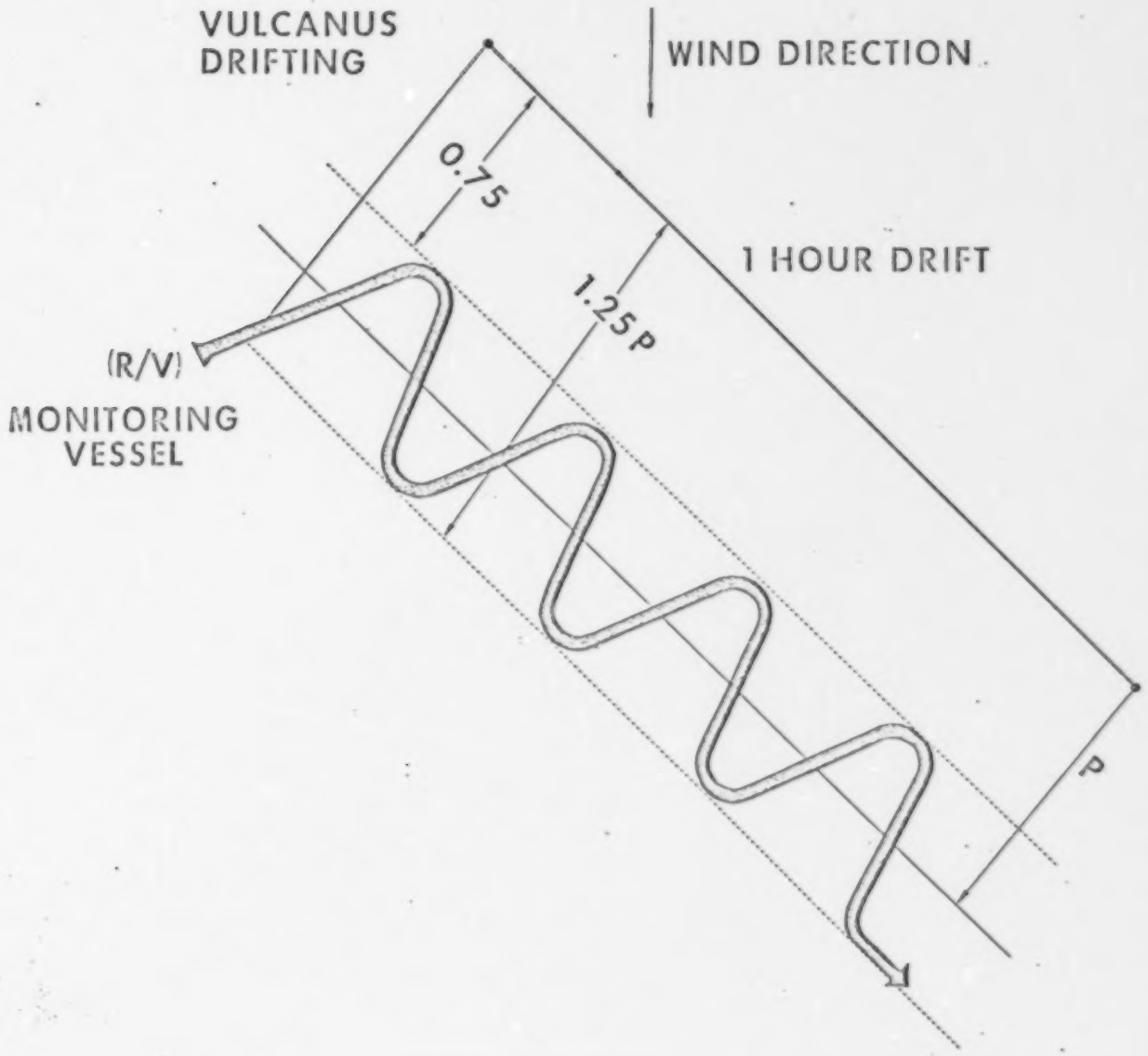
III. Operational Schedule

Data collected over a variety of climatic conditions is required under both day and night conditions. While it is not essential for marine environmental monitoring to be done during all the time of burning, it is essential that the collection of data be such that the full spectrum of conditions under which burning occurs be sampled to the greatest extent possible.

In a practical sense, this means sampling should be done during wind speeds of from 10 to 30 knots, and under rainy as well as no precipitation conditions. At wind sppeds of more than 30 knots, it is not likely that the HCl monitor could be operated successfully, assuming that it was possible to sample effectively in the sea state at that wind speed.

FIGURE 3

LONG RANGE EFFECTS SAMPLING PATTERN



▨ PHYTOPLANKTON AND ZOOPLANKTON TOWS

R/V SPEED AND COURSE SET BY RATE OF DRIFT AND PRACTICABLE TOW SPEED

P = DISTANCE FROM VULCANUS AT HIGHEST OBSERVED PLUME CONCENTRATION

Also, under rainy conditions at high wind speeds, it would not be safe to approach VULCANUS closely enough to sample the area in which scrubbed-out contaminants entered the water, assuming that they would not be so widely dispersed in a driving rain as too be undetectable.

In view of the data which were obtained during the first burn, the order of priority in which observations should be made are:

1. Rain, wind speeds 10 knots or less.
2. No rain, wind speeds 10 knots or less.
3. No rain, wind speeds of about 20 knots.
4. Rain, wind speeds of about 20 knots.

At each of these conditions at least duplicate plume identification runs and water sampling runs should be made if possible, preferably under both day and night conditions. It is recognized, of course, that weather conditions must be accepted as they are found and that it is likely that all of the above conditions may not be found during any one burn. The time on station of the monitoring vessel should be scheduled based on weather predictions, so as to conduct the on-site operations over as broad a range of weather conditions as possible.

IV. Control Stations

For each set of sampling stations taken on one run, suitable control stations will be occupied upwind of the VULCANUS and at least 3 miles away. Control station samples will be treated precisely as the samples taken in impacted areas.

APPENDIX B

Method for Alkalinity Determination

The method for analysis is a potentiometric titration which involves mathematical determination of end points.

For total alkalinity the only end point of concern is the HCO_3^-. The first end point or $CO_3^=$ end point is of no concern.

Materials:

1. 0.10 M HCl (high purity standard acid)
2. Gilmont 2.5 ml high precision buret (accuracy 0.02%)
3. Corning digital pH meter with combination electrode

Procedure: A 5.0 ml sample is titrated with 0.10 M HCl. This is accomplished by first obtaining the millivolt reading (from the pH meter) of a sample to which no HCl has been added. Next 0.01 ml of 0.1 M HCl is added (with a Gilmont buret) and the respective change in millivolts is measured. A series of 0.01 ml increments of 0.1 M HCl is then added to the sample and after each increment the respective change in millivolts is noted. As the HCO_3^- (or total alkalinity endpoint) draws near there will be a greater and greater change in the millivolt reading. As this begins to occur the increments of acid to be added is changed from 0.01 ml to 0.005 ml (for greater accuracy). When the endpoint is surpassed progressively smaller changes in the millivolt reading will be observed as acid is added.

A series of large changes in the millivolt readings (when the acid increments are added) is selected on either side of the end point. Then first and second derivatives (Δ millivolts/Δ Vol. acid; Δ^2 millivolts/Δ vol. acid^2) are determined among these points. From this, the volume of acid needed to reach the endpoint is determined. This volume of acid (in ml) when multiplied by its normality gives the total number of milliequivalents of (H^+) used to reach to total alkalinity endpoint. Since 5.0 ml of sample is used, the number of meq. of (H^+) must be multiplied by 200 to give meq. (H^+)/l.

The precision of this method is $\pm$ .01 meq (H^+)/l.

Method for Chlorinity Determination - Vulcanus Samples

The Mohr titration is based on the differential solubilities of the Cl^- ion (and other halides) and the $CrO_4^=$ ion with the Ag^+ ion. Initially the chloride ions (and the other halides) are precipitated by silver due to its lower solubility. When the chloride has been depleted, the $CrO_4^=$ ion reacts to form a red precipate signalling the end point of the titration. Samples are compared with Copenhagen standard sea water to obtain chlorinity values.

Reagents:

1. Silver nitrate $AgNO_3$ (~0.6N)
2. Chromate indicator: 4.2 g K_2CrO_4 + 0.7 g $K_2Cr_2O_7$ in 100 ml deionized water
3. Sodium bicarbonate ($NaHCO_3$)

Method: Twenty-five ml of deionized water, 1 ml of sample, and a micro spatula of $NaHCO_3$ (to buffer pH in 7-10 range) are added to a 125 ml Erlenmeyer flask. The flask is placed on a magnetic stirring plate and a stirring bar is added to the flask. Silver nitrate solution is slowly added to the sample solution from a 10 ml burette. The sample solution is continually stirred. Dropwise addition of silver nitrate is continued until a faint reddish-brown color was detected. This signals the end point of the titration and the volume of $AgNO_3$ used is recorded to the nearest 0.01 ml.

A standard working curve is generated by following the above procedure using Copenhagen Standard Sea Water (19.3755 ppt Cl) and dilutions thereof. Sample values are then calculated relative to the standard. The precision of this method is $\pm$0.03 ppt.